



New uperwetting Surfactants

FOR COATINGS APPLICATIONS

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Surface active agents, or surfactants, are materials that can adsorb onto surfaces or at interfaces and lower the surface or interfacial-free energies of aqueous-formulated systems. Traditionally, surfactants have a characteristic molecular structure that includes a water-loving (hydrophilic) head and an oil-loving (lipophilic) tail. Because of their amphiphilic nature, surfactants will migrate to and accumulate at interfaces and reduce surface and interfacial tensions, even when used at very low concentrations. Conventional surfactants have a polar or ionic hydrophilic head group connected to a hydrophobic, hydrocarbon tail group. In contrast, a particular type of specialty surfactant structure, termed Gemini, has two hydrophobic tails connected to two hydrophilic head groups on the same molecule. As shown in *Figure 1*, each half of the “twin” surfactant is joined together by a spacer group, forming the Gemini structure. Because of their unique molecular architectures, these Gemini surfactants are much more surface active than their “monomeric” components.¹ Gemini surfactants are often used in waterborne coating, ink, and adhesive formulations for both dynamic surface tension reduction and foam control.

Wetting of a surface is a process in which a fluid spreads or flows over another surface when the spreading coefficient, S , is positive.² In a waterborne paint or coating, this wetting phenomenon can occur in many places throughout the system. Although wetting agents (i.e., surfactants designed to facilitate wetting) primarily aggregate at the air/liquid interface, wetting can also occur at air/solid, liquid/solid, and liquid/liquid interfaces (see *Figure 2*). Many surfactants can act to facilitate substrate and particle wetting by reducing the surface tension of the formulation to a level that is equal to or lower than the surface tension of the substrate being coated. As the surface tension of water is 72 mN/m and typical coating substrates have surface energies in the realm of 35–45 mN/m, surfactants must be used to decrease the surface tension of the water-based paint to allow it to flow smoothly onto the substrate. Additionally, in order for wetting to occur, the contact angle, θ , must be less than 90°; contact angles greater than 90° result in beading of the coating on the substrate. *Figure 3* illustrates how choosing a surfactant that can lower the surface tension of the coating to below the surface energy of the substrate results in a final film with excellent wetting. In some cases, surface energies of substrates may be less than 35 mN/m and present a significant

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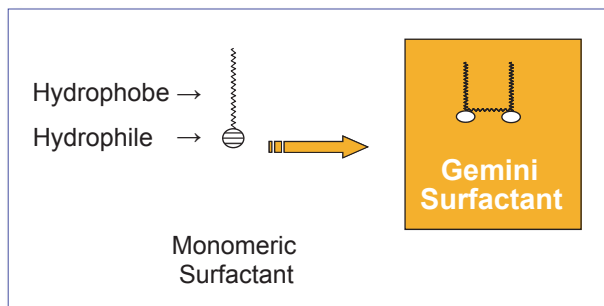


Figure 1—Conventional and Gemini surfactant structures.

problem to the applicator. When this occurs, two pathways need to be followed. First, the substrate may be treated to raise the surface energy, making it easier for the coating to wet out the surface. When this is not a viable option, the formulator is then forced to look at a stronger set of surfactants, including superwetters, to achieve the low surface tensions needed to wet out the substrate.

TRADITIONAL SURFACTANTS

Surfactants can be classified in several ways. They may be nonionic, anionic, or cationic in nature, and the choice of which type to use is often determined by the application and other components in the formulation. The largest and most commonly used class of surfactants, the anionic surfactants, include chemistries like alkylbenzene sulfonates, fatty acid soaps, and dialkyl sulfosuccinates.³ Although these surfactants offer excellent wetting at a relatively low cost in use, their main drawback is their tendency to foam in coatings, thus requiring the formulator to include strong defoaming agents in the system, which can lead to film defects and aesthetic issues. Nonionic surfactants, many of which are based on polyethoxylated materials, can be excellent wetting agents and emulsifiers.³ This group contains the previously mentioned Gemini surfactants and their derivatives, as well as siloxane-based surfactants and fluorosurfactants. The final and smallest group, the cationic surfactants, is used less often in coatings applications since they will react with any anionic species in the system; however, they are sometimes used as solid particle dispersants or emulsifiers.³ All three types of surfactants can offer excellent wetting, but they perform differently when subjected to dynamic conditions and exhibit different foam profiles.

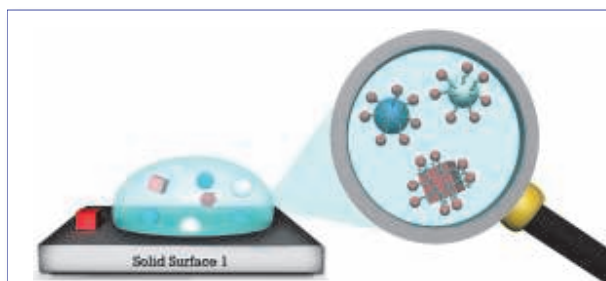


Figure 2—Where wetting occurs in waterborne coatings: air/solid, liquid/solid, and air/liquid interfaces.

SUPERWETTING SURFACTANTS

Waterborne systems, like those used in architectural coatings, have high surface tensions due to the high surface tension of water. As a result, surfactants are required to lower surface tension to achieve good pigment wetting needed for efficient grinds, as well as to achieve good substrate wetting required for acceptable appearance and performance of the applied coating. This becomes particularly challenging with lower-VOC coatings, which are now formulated to well below 100 g/L—and even down to 0 g/L—with less solvent to help flow, leveling, and appearance of the coatings. In such cases, the formulator may employ the use of superwetting surfactants to reach the desired level of wetting. Superwetting surfactants can be siloxane-based or organic in nature and they differ from traditional surfactants in several ways. The hydrophobes of superwetting surfactants are very compact, which allows them to adsorb efficiently and pack well at interfaces. They are also capable of reducing equilibrium surface tensions to below 28 mN/m and achieving extremely fast wetting times. Additionally, as can be seen in *Figure 4*, superwetting surfactants attain low contact angles on low surface energy substrates.⁴

Organic Superwetting Surfactants

Organic superwetting surfactants are able to achieve reasonably low equilibrium and extremely low dynamic surface tensions; therefore, they are often excellent alternatives to traditional siloxane and fluorosurfactants. While siloxane and fluorosurfactants can achieve very low equilibrium surface tensions, their dynamic surface tension performance is much poorer because they are unable to quickly migrate to the newly created

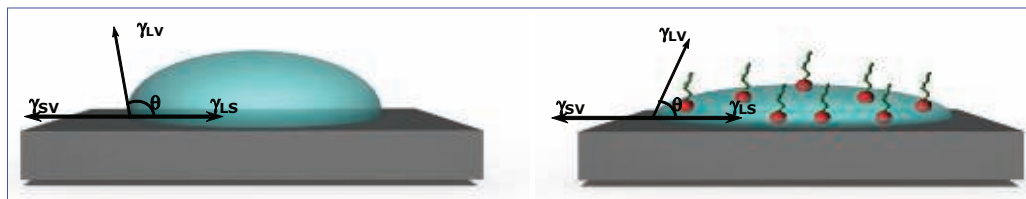


Figure 3—Wetting agents facilitate substrate and particle wetting. γ_{sv} , γ_{sl} , and γ_{lv} are solid-vapor, solid-liquid, and liquid vapor interfacial tensions.

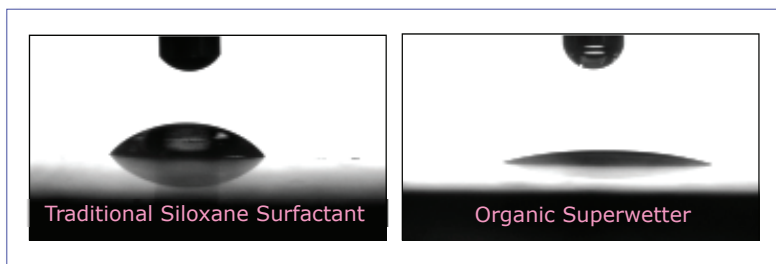


Figure 4—Wetting of a traditional siloxane surfactant vs organic superwetter. 0.1 wt% aqueous solution, oily metal surface, 10 sec wetting time, 23°C.

interfaces under dynamic conditions and maintain that low surface tension state. When used in a waterborne formulation, traditional siloxane-based and fluorosurfactants will migrate to the air/coating interface, as they tend to be organophobic. This may lead to recoatability issues if a second layer of coating is applied. In contrast, organic superwetting surfactants maintain their low dynamic performance even during high-speed coating processes. One other benefit to using organic superwetting surfactants is that they are generally more compatible with most coating systems, have no or minimal foam stabilization, and present no issues regarding recoatability that may be observed with the siloxane-based and fluorosurfactants. *Figure 5* highlights the equilibrium and dynamic surface tension performance of some organic superwetters compared to siloxane-based and fluorosurfactants.

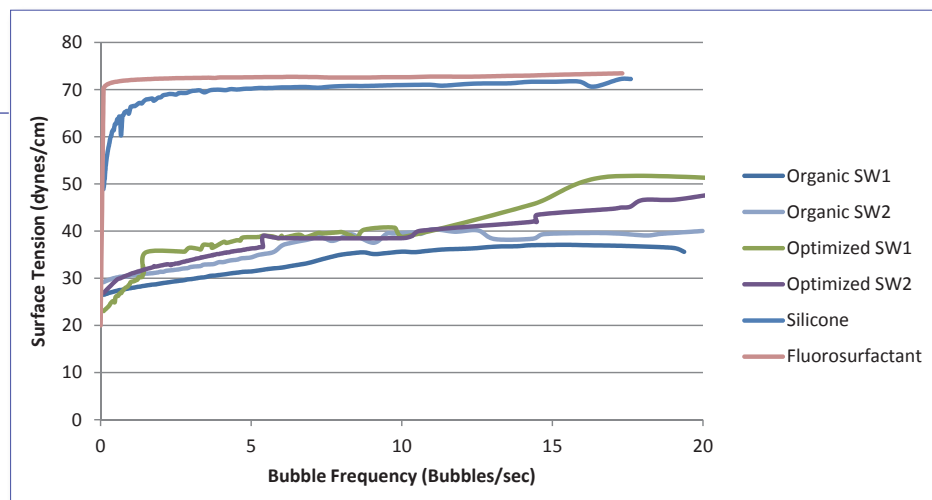
Optimized Siloxane-based Superwetting Surfactants

Many waterborne resin systems suffer from application limitations that can only be effectively eliminated by using high quality surfactants and defoamers. In particular, poor substrate wetting, edge retraction, pinholing, and other defects result in high product failure rates that are costly to the manufacturer. Choosing the right surfactant that provides effective wetting and leveling while

minimizing foam improves the overall performance of the coating formulation. It is well known that siloxane-based surfactants have the ability to spread on surfaces and promote excellent flow and leveling, often exceeding the flow and leveling achievable with organic superwetting surfactants. However, it has also been shown that organic superwetting surfactants are capable of effectively migrating to newly created interfaces to maintain low surface tension levels during application—a benefit not achievable with a traditional siloxane surfactant.⁵

Recently, optimized siloxane-based superwetting surfactants have been developed; these new products exhibit the outstanding spreading, flow, and leveling usually associated with siloxanes, as well as the low-foam, dynamic wetting benefits attributed to organic superwetting surfactants. *Figure 5* compares the dynamic surface tension performance of the organic superwetters, a siloxane-based surfactant, a fluorosurfactant, and the new optimized siloxane-based superwetters. Because they possess both the siloxane and the organic functionalities, these optimized superwetting surfactants provide superior flow and leveling and low-foam wetting. Additionally, these surfactants offer improved formulation compatibility and do not suffer the recoatability issues that may be seen with traditional siloxane surfactants. When trying to coat a very hydrophobic surface such as plastic or wood, particularly when spray-applying a coating, it is critical that the wetting package be able to perform while under dynamic shear and then again when the coating flows and levels across the substrate. The unique structure of these optimized siloxane-based surfactants allows the formulation to effectively wet the surface of the substrate and flow evenly across the surface. *Figure 6* illustrates how these new siloxane-based superwetting surfactants meet the targeted goal with respect to equilibrium and dynamic surface tension reduction.

Figure 5—Dynamic surface tension comparison of aqueous solutions containing 0.1 wt% surfactant (measured using a Krüss BP-II Bubble Tensiometer).



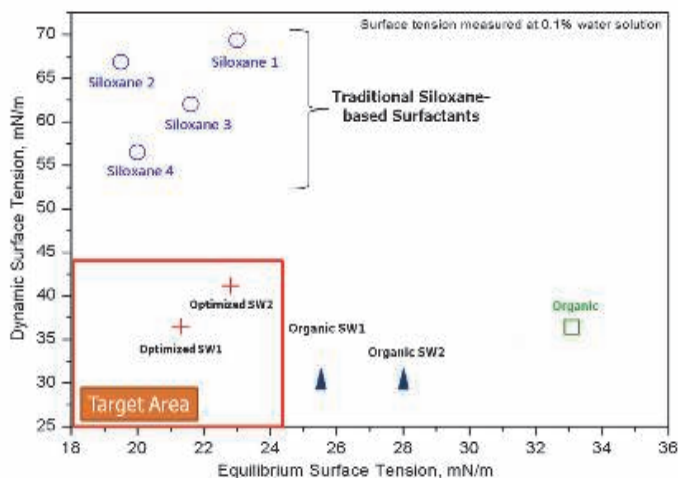


Figure 6—Equilibrium surface tensions vs dynamic surface tensions for select surfactants.

APPLICATIONS DATA

Plastic Coatings

When coating hydrophobic substrates with very low surface energies, like plastic, perfect wetting is difficult to achieve, particularly when spray-applying the coating. Efficient dynamic and equilibrium surface tension reduction are key factors in affecting final wetting performance. To illustrate the effectiveness in wetting performance of the new optimized siloxane-based superwetters, a two-component polyurethane coating crosslinked with isocyanate was prepared and applied to a silicone release liner. The formulation can be found in *Table 1*. As seen in *Figure 7*, with no surfactant, the system completely de-wets on the release liner. Using the Organic SW1 or a siloxane-based surfactant also results in poor wetting and defects in the film. By incorporating Optimized SW1, excellent dynamic and equilibrium surface tension reduction is achieved, resulting in excellent wetting with no defects.

Table 1—2K Polyurethane Waterborne Plastic Coating

Ingredient	Weight in grams
Bayhydrol® AH XP 2741, 40%, s.f.	36.0
Dimethylethanolamine, 10% in D.I. water	4.0
Water	41.0
Butyl glycol	2.0
Surfactant	0.2
Acrysol® TT-935, 6% in D.I. water	6.0
Bayhydur® 304	8.0
Propylene glycol monomethyl ether acetate	0.6

Table 2—Blue Printing Ink Formulation

Ingredient	Weight in grams
Joncryl® 624	45.0
Joncryl 60	15.0
BFD-1121 Blue dispersion	30.0
Water	9.0
Airase® 4500 defoamer	0.20
Wetting agent	0.50

Printing Inks

The multifunctional benefits of exceptional wetting and defoaming of an organic superwetter, designated as Organic SW 1, can be seen in *Figure 8*. A blue packaging ink formulation was prepared, as shown in *Table 2*, and applied to low-density polyethylene using a 200P handproofer. When compared to a traditional organic surfactant, a fluorosurfactant, and a siloxane-based surfactant, Organic SW 1 offers superior wetting and printability, while maintaining excellent foam control when used to print on film substrates such as oriented polypropylene or high-slip polyethylene. The organic superwetter's ability to lower the dynamic surface tension under high press speeds results in a film

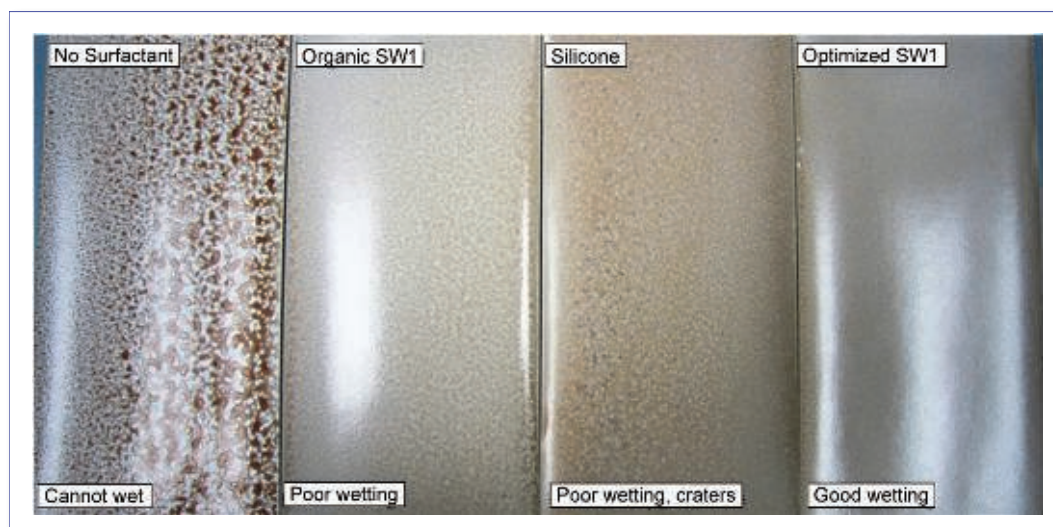


Figure 7—2K polyurethane waterborne clearcoat based on Bayhydrol AH XP 2741 spray applied to silicone release liner.

Figure 8—Blue packaging ink printed on low density polyethylene.

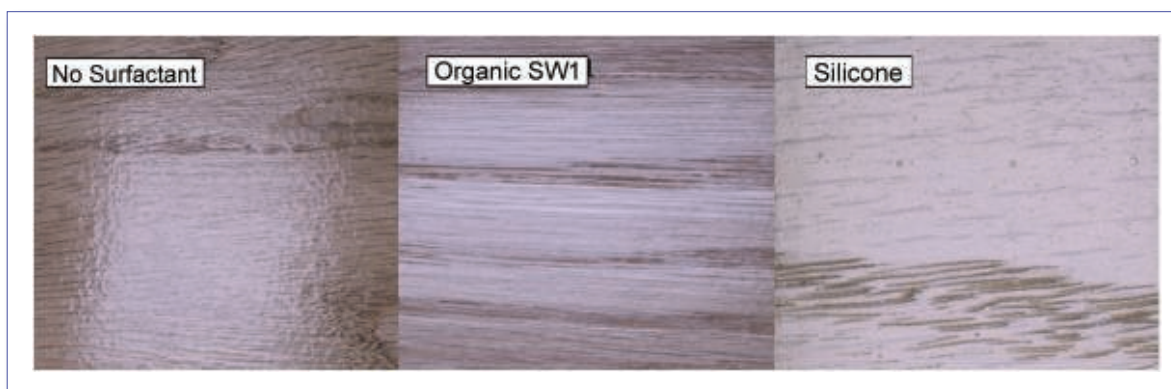
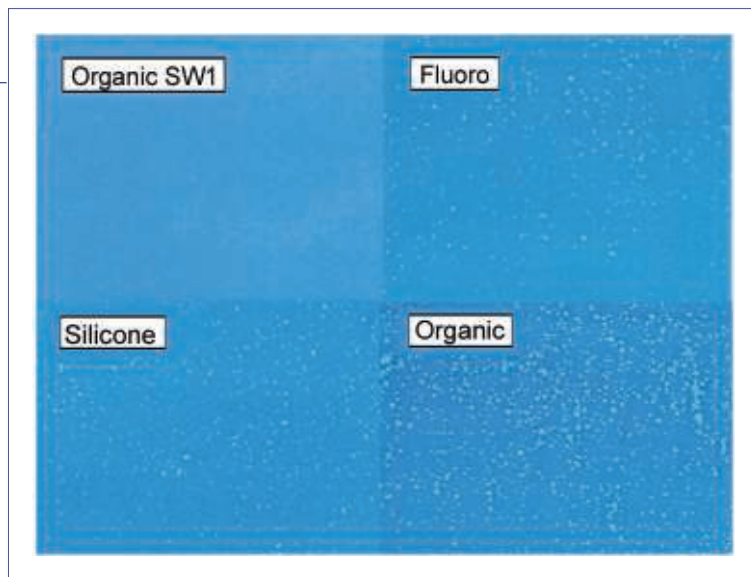


Figure 9—Polyurethane acrylic hybrid coating applied to red oak.

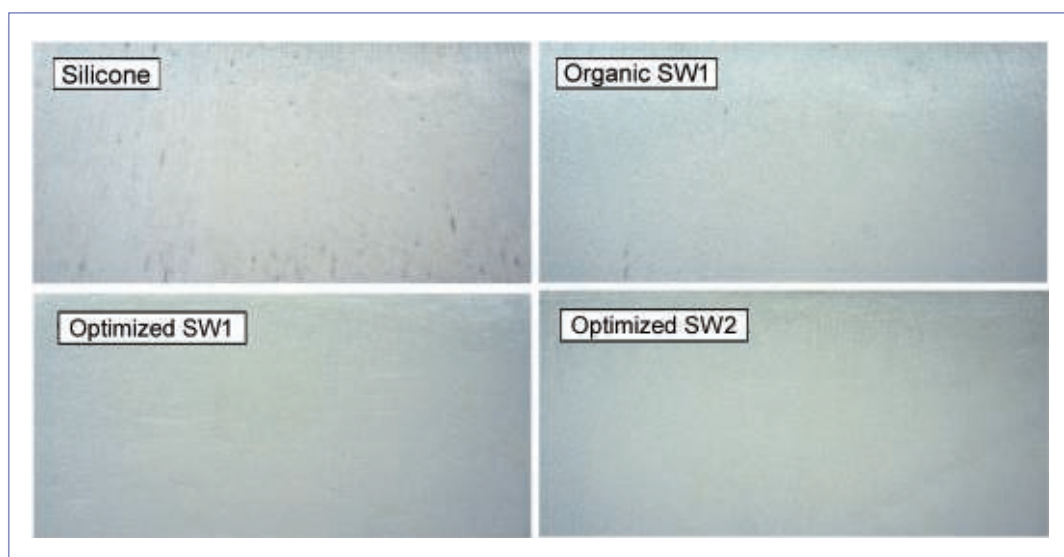


Figure 10—Acrylic wood coating containing 0.2 wt% surfactant spray applied on wood.

Table 3—PU-Acrylic Hybrid Wood Coating on Red Oak

Ingredient	Weight in grams
Hybridur® 870	78.5
Dowanol® DPNB	4.0
Tafigel® PUR50	0.5
Water	15.8
Surfynol® DF-58	0.2
Wetting Agent	1.0

print with zero defects, while the other surfactants exhibit microfoam and pinholing defects. In this particular case, it can be clearly seen that the organic superwetter provides sufficient and necessary wetting to coat the plastic film. An optimized siloxane-based superwetter could also be used; however, the superior performance is not needed in this particular formulation to achieve adequate wetting.

Wood Coatings

Wood substrates are inherently difficult to wet out due to the porosity of the substrate, surface contaminants such as glue or sap, and irregularity in the surface roughness. As the coating flows over the surface of the wood, penetration of the coating into the substrate occurs; this can lead to surface imperfections from both inadequate wetting and foam generation. When the coating penetrates into the wood and wets out the grain, air is displaced, which rises to the surface and can become trapped in the dried film. Selecting a wetting agent that offers excellent flow and leveling as well as foam control is critical for a high-quality finish. *Figure 9* illustrates a waterborne wood coating based on a polyurethane-acrylic hybrid polymer system—Hybridur® 870, brush-applied on red oak. In this formulation, shown in *Table 3*, when no surfactant is added to the system, severe orange peel is seen in the coating. In comparison, when incorporating Organic SW1 or a siloxane-based surfactant, the surface appearance is greatly improved. However, only Organic SW1 can migrate quickly to the newly formed interfaces during application and not only lower the surface tension but also eliminate any foam generated by the wetting of the substrate. The siloxane surfactant offers excellent wetting but stabilizes foam which is still apparent in the dried coating.

To demonstrate the additional benefits seen with the new optimized siloxane-based superwetting surfactants, a second formulation was prepared and tested. *Table 4* details the formulation based on Craymul® 2173. This formulation was prepared and spray-applied onto wood at a wet film thickness of 100 µm. As shown in *Figure 10*, compared to the siloxane-based surfactant and Organic SW1 surfactant, the optimized siloxane-based superwetter surfactants, Optimized SW1 and Optimized SW2, show improved crack filling and foam control when spray-applied onto the wood surface. The ability

Table 4—Spray-Applied Acrylic Wood Coating

Ingredient	Weight in grams
Craymul® 2173	80.0
Acrysol® RM-8W	1.2
Dowanol® DPnB	7.0
Surfynol DF-62	0.25
Surfynol 104DPM	0.3
Water	7.7
Wetting agent	0.2
Aquacer® 513	2.5
Acrysol RM2020	0.5
White color paste	15.0

of the optimized siloxane-based superwetters to migrate faster than conventional surfactants to problem areas to lower the surface tension and the ability of these superwetters to then aid in the flow and leveling of the final coating is clearly apparent in *Figure 10*.

CONCLUSIONS

Surfactants diffuse to and adsorb at surfaces to reduce surface tension. This phenomenon is particularly critical for waterborne systems requiring excellent wetting and flow and leveling on difficult-to-wet surfaces. Superwetting surfactants greatly reduce surface tensions to low-energy levels and improve wetting on very low-energy, hard-to-wet surfaces like oily metal, low-energy plastics, and porous wood. New optimized siloxane-based superwetting surfactants have been developed to offer the formulator the ability to achieve low dynamic surface tensions with minimum foam generation while promoting excellent flow and leveling for waterborne coatings. **CT**

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